

Exhibit 64

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Optimal Treatment Condition for Changing Characteristics of Naturally Occurring Asbestos

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ABSTRACT

Naturally occurring asbestos (NOA) refers to asbestos found as a natural component of rocks and soils. The purpose of this study was to determine effective methods for changing the characteristics of NOA. Unprocessed chrysotile-containing soils and rocks were treated using heat (700–1100°C for 1–3 hours) and combination (100–250°C, 0.3–1.0 M oxalic acid for 1–3 hours) methods. A polarized light microscope (PLM) and field emission scanning electron microscope (FE-SEM) with an energy-dispersion spectrometer (EDS) were used for the analysis of both untreated and treated samples. While PLM analyses revealed gradual change in optical properties in both heat and combination treatments, SEM/EDS analyses revealed morphological and chemical changes under conditions of combination treatment. The elemental composition of combination treated samples showed low levels of magnesium and high levels of silicon compared to untreated samples. The optimal treatment condition was 1 M oxalic acid at 250°C temperature for 1 hour. Combination treatment resulted in changes in NOA characteristics at lower temperatures than did heat treatment alone.

Keywords: Asbestos; NOA; Combination treatment; Oxalic acid; PLM.

INTRODUCTION

Asbestos was formerly widely used as a raw material in construction and industry due to its high strength, non-flammability, and low cost. However, asbestos is classified as a carcinogen by the International Agency for Research on Cancer (IARC) (Group 1), the American Conference of Governmental Industrial Hygienists (ACGIH) (A1) and so on. Naturally occurring asbestos (NOA) refers to the mineral as a natural component of soils or rocks, as opposed to asbestos in commercial products, mining, or processing operations. NOA can be released from rocks or soils by routine human activities, such as construction, or by natural weathering processes (Yoon, 2009).

In epidemiological studies, a high incidence of asbestos-related disease was found among mine workers in the 1980s, and among the residents of Libby, Montana (USA), in late 1999 (Ross and Nolan, 2003). Accordingly, the dispersion

of NOA in the environment became an increasingly important issue, although asbestos concerns have focused mainly on occupational problems. NOA may be found not only in large commercial sites and active, closed, or abandoned mines but also in small noncommercial deposits throughout mountain ranges (Lee *et al.*, 2008). NOA exposures typically occur at lower levels than occupational exposures, and at irregular intervals, regardless of the age and background of individuals (Melious, 2012). Human exposure to NOA may be a particularly serious problem because it occurs in various locations, forms, and quantities.

Although many studies on the treatment of asbestos have been performed, most research focused on asbestos-containing materials (ACMs) such as ceiling tiles, roofing slates, etc. Treatment methods included dissolution in acids, hydrothermal treatment, mechanochemical treatment with high-energy milling processes, fiber melting, and vitrification using plasma technology (Kusiorowski *et al.*, 2012). However, existing methods are costly and energy intensive, and whether the treated asbestos is completely detoxified is questionable.

In Korea, most asbestos wastes are processed in solidified form after being packed into polyethylene bags, or thermally treated at high temperatures and buried in designated landfill

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facilities (Park *et al.*, 2013). However, these methods have problems due to the limited land area available and are not appropriate for treating large quantities of asbestos waste. The cost is approximately 70 billion won if solidifying or melting methods are used after classifying designated wastes based on the content of asbestos (Ministry of Environment, 2011). To address this issue, various methods have been suggested, but development of safer and more efficient and treatments that address the problems of high cost and secondary exposure post-treatment is necessary.

The toxicity of asbestos is due to various factors. The key human disease-causing mechanisms are unclear. Of the physical factors, particle size and shape determine the rate of deposition in the human lung. Surface roughness also affects carcinogenesis, chemical mechanisms, and dissolution rate. The major chemical factors may be related to the surface chemical composition and active surface states (Fubini and Arean, 1999). It is hypothesized that magnesium originating from chrysotile reacts intracellularly, thereby causing cytopathogenicity (Gulumian, 2005). Therefore, treatment methods should alter both the chemical and physical properties of asbestos to facilitate its detoxification (Nam *et al.*, 2014).

Many studies have aimed to identify effective asbestos treatment methods. However, most concerned ACMs and focused on treatment at high temperatures. After thermal treatment of asbestos at 600–650°C, chrysotile showed the dehydration (Hashimoto *et al.*, 2006; 2008). For complete recrystallization, asbestos needed over 800°C of heat (Kusiorowski *et al.*, 2012). Combination treatment of asbestos with oxalic acid and ultrasound was effective in decomposing asbestos (Turci *et al.*, 2010), but the subjects were asbestos in water and should be treated for long time over 12 hours using this technology. Another combination treatment with sulfuric acid and heat (Nam *et al.*, 2014) also needed at least 10 hours and it concerned only slates which classified as ACMs. There is a lack of experimental data on detoxifying NOA and identifying effective treatment methods. Also, to the best of our knowledge, there is no studies on comparing heat and combination treatment directly. Therefore, the aims of this study were to compare the effects of thermal and thermochemical treatments and to identify the optimal treatment condition for NOA to reduce time and cost.

MATERIALS AND METHODS

Experimental Samples

A total of six field samples were collected from Hongseong County in Chungnam Province (Korea) and Ulsan City (Korea), which are known tectonic divisions and serpentinite outcrops in Korea, and Quebec (Canada), which is known

NOA locations (asbestos mines). The basic characteristics of the samples are listed in Table 1.

All NOA samples were dual-packed and experiments were conducted in a laboratory equipped with protective equipment suitable for asbestos, including high-efficiency particulate absorption (HEPA) filter-equipped hoods, etc. To reduce experimental error, each test was conducted with samples of a fixed weight (300 mg) or size (2 cm × 2 cm × 2 cm). All samples were dried at room temperature and used without pre-treatment. Asbestos contents of all samples were > 10%.

Experimental Procedures

In this study, we attempted to alter the characteristics of asbestos using heat and acid treatments. Because acid-only treatment showed no significant effect after 48 hours (Moon, 2014), the effects of heat and combination treatments were evaluated. To identify the optimal treatment conditions for NOA, various temperatures, times, and acid concentrations were used.

Heat Treatment

Heat treatment is the most common asbestos decomposition process used. In previous studies, chrysotile changed physically at 600–800°C (Candela *et al.*, 2007) and its optical properties were affected by treatment for 3 hours at 700°C (Moon, 2014).

Based on prior studies, the following treatment conditions were used: (1) 700°C, 800°C, 900°C, 1000°C, and 1100°C for (2) 1, 2, or 3 hours. Samples were heated in an electric furnace (WiseTherm, Daehan Scientific, Korea) after being placed into a crucible. All soil samples were 300 mg and all rock samples were 2 cm × 2 cm × 2 cm in dimensions.

Combination Treatment

A graphite block (ECO-PRE, ODLAB, Korea) was used to perform simultaneous heat and acid treatments. Preliminary results showed that the properties of asbestos fiber changed following treatment at 200°C with 0.3 M oxalic acid for 1 hour (data not shown). Therefore, the following treatments were performed: (1) 100°C, 150°C, 200°C, and 250°C, (2) 1, 2, or 3 hours, and (3) 0.3 M, 0.5 M, or 1 M oxalic acid. Samples consisting of either 300 mg of soil or rock of dimensions 2 cm × 2 cm × 2 cm were placed into a Teflon vessel. Oxalic acid (50 mL) was transferred into the vessel and the pressure lid was closed loosely to prevent evaporation of oxalic acid. The treated samples were separated by being passed through mixed cellulose ester (MCE) filters (0.8-μm pore size; 47-mm diameter) using vacuum filtration while rinsing with distilled water. The filtrate residues were placed into Petri dishes, and dried for at least 24 hours.

Table 1. Basic characteristics of the asbestos samples.

Asbestos type	Sample number	Sampling location	Number of samples
Chrysotile-containing soil	S-1, S-2, S-3	Hongseong (Korea)	3
Chrysotile-containing rock	R-1	Hongseong (Korea)	1
Chrysotile-containing rock	R-2	Ulsan (Korea)	1
Chrysotile-containing rock	R-3	Quebec (Canada)	1

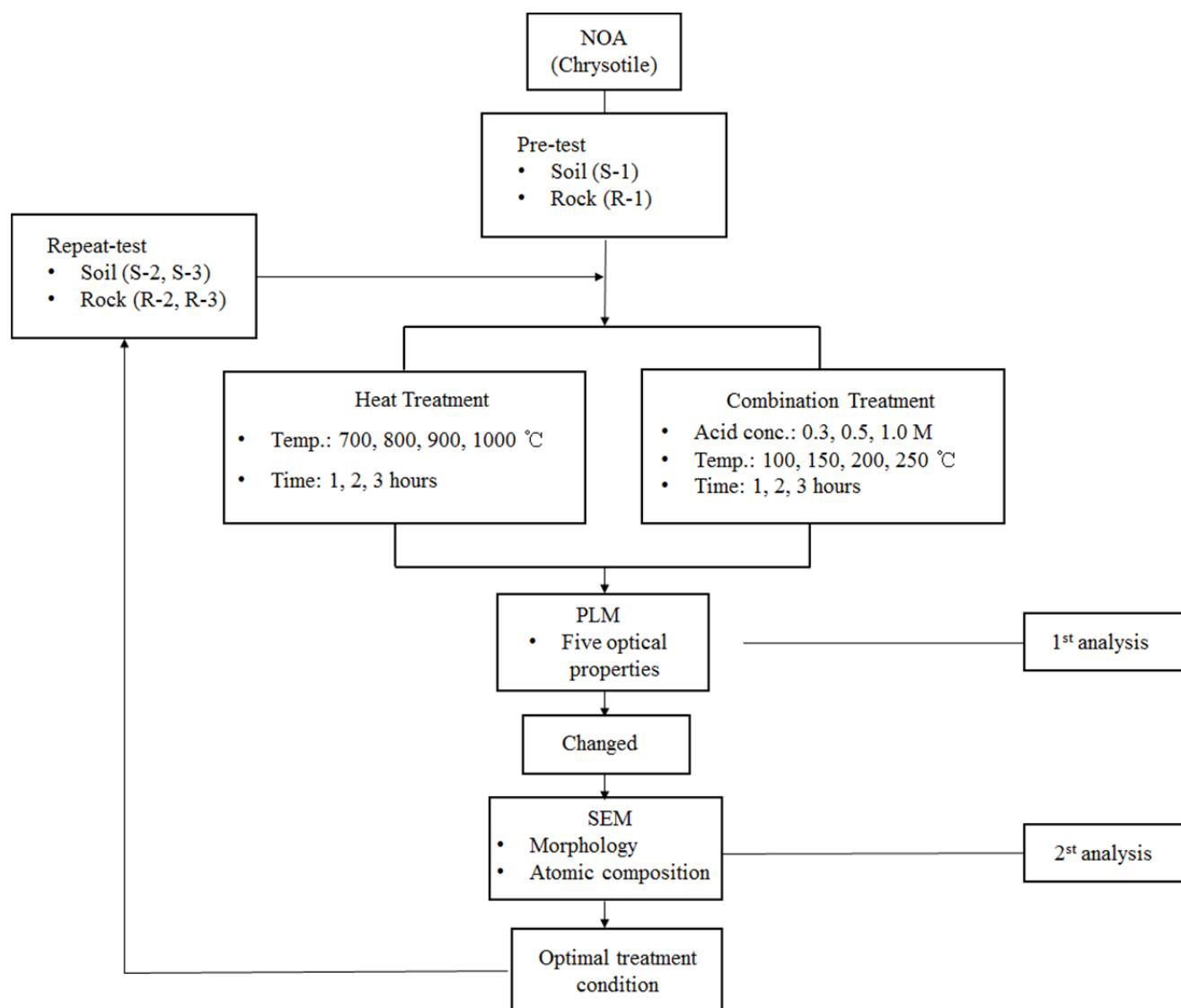


Fig. 1. Outline of study protocol.

Analytical Techniques

PLM Analysis

Polarized light microscopy (PLM, BX51, Olympus, Japan) was used for qualitative analysis of the target substances before and after treatment (Zarubiieva *et al.*, 2013). Asbestos fibers were extracted from the samples and pre-treated using a refractive reagent (refractive index [RI] = 1.550, Cargille Laboratories, USA) on a glass slide topped with a cover glass. Then, the fibers were analyzed using a polarized light microscope with reference to the National Institute of Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM) Method No. 9002. Morphological and optical properties such as [RI], pleochroism, sign of elongation, extinction, and dispersion staining [DS] were identified in NOA samples. All samples were analyzed (objective lenses = 10×, ocular lenses = 10×) in triplicate. The average thickness (width) of analyzed fibers was ~50 μm.

Chrysotile has no pleochroism, which is defined as a difference in color according to mineral orientation (north-

south, east-west) under conventional illumination with only the polarizer in the optical light path. Under crossed polar with the insertion of a first-order red retardation plate, a difference in phase is termed a sign of elongation. Chrysotile has a positive sign of elongation, in which the length refractive index value of the fiber is of greater magnitude than the width refractive index. A bright white pattern was observed when removing the first order red plate under crossed polar, and a parallel (to the cross hair) total extinction of the fiber was observed when rotating the stage. The angle of extinction is also used to identify asbestos, and chrysotile has parallel extinction (extinction angle = 0°). Under polarized light with insertion of the DS objective, the fibers were observed using an objective that has a disk placed in the back focal plane so that only the dispersed light is observed. In the case of chrysotile, fibers oriented in the north-south direction exhibit a blue-magenta color, while those in the east-west direction exhibit a light blue color.

Refractive index (RI) is defined as the relative ratio of velocity in a vacuum ($V_{\text{vac}} \doteq 3 \times 10^{10} \text{ cm s}^{-1}$) to velocity in

a medium (V_{sub}). It is the most important optical property for PLM analysis, and asbestos can be analyzed by measuring two RIs (n_{\parallel} , n_{\perp}) according to light vibration direction (length, width) within a fiber. In this study, a DS method was used for measuring the RIs; the procedure follows.

Assuming that the polarizer is parallel to the east-west direction of the cross hairs, rotate the microscope stage until a fiber bundle is parallel to the east-west cross hair. A range of DS color is usually displayed; ensure that the DS color that gives the highest RI (n_{\parallel}) is observed; that is, the DS color corresponding to the shortest matching wavelength. For example, if the DS color ranges from purple to red-purple, choose red-purple. Rotate the microscope stage 90° and then repeat the steps to determine another RI. In this case, ensure that the DS color that gives the lowest RI (n_{\perp}) is observed; that is, the DS color corresponding to the longest matching wavelength. For example, if the DS color ranges from blue to light blue, choose light blue.

SEM/EDS Analysis

A field emission scanning electron microscope (FE-SEM, MIRA II LMH CS02, TESCAN, Czech Rep.) equipped with an energy dispersion spectrometer (EDS, AnalyZer Model 550i, TESCAN, Czech Rep.) was used to assess the microstructure and chemical composition of asbestos. The presence or absence, destruction or non-destruction, and elemental change or non-elemental change of untreated and treated asbestos fibers were examined. The samples were fixed on carbon tape attached to the surface of an aluminum mount and coated with platinum (Pt) for SEM analysis.

All samples were analyzed (magnification = 2,000 \times ; SEM HV: 15.00 kV; WD: 15.00 mm) three times, and the average of each result was used. Because of the marked variations in magnesium and iron, silicon was the main criterion used to identify changes.

Statistical Analysis

The results of three repeated analyses are expressed as means \pm standard deviation. Student's t -test and the paired t -test were carried out using SPSS 20.0 (SPSS, Chicago, IL, USA). SigmaPlot 10.0 (Systat Software, Inc., USA) was used

to interpret graphs. A value of $P < 0.05$ was taken to indicate statistical significance.

RESULTS

PLM Analysis

Regarding heat treatment, the optical properties of chrysotile-containing soil changed at 1000°C , but the properties of chrysotile-containing rock showed no significant change. PLM analyses showed that sign of elongation and DS of chrysotile-containing soil started to change at 800°C , and completely changed at 1000°C (Table 2). However, the sign of elongation of chrysotile-containing rock was unaffected at 1000°C . Chrysotile soil and rock started to show color after heat treatment, but the extinction showed no change under any of the heat treatment conditions.

The RIs of chrysotile-containing soil tended to increase according to temperature, and dramatically increased at 1000°C (Fig. 2). The width RI value of the fiber (Fig. 2(b)) tended to show a greater increasing pattern than the length RI (Fig. 2(a)). There was little change according to time.

Regarding the combination treatment, the optical characteristics of NOA started to change following treatment with 1 M oxalic acid at 250°C for 1 hour. There were no changes following the combination treatment at 100°C , 150°C , or 200°C (data not shown). This study focuses on the effects of the combination treatment at 250°C .

Chrysotile-containing soils and rocks were treated with 0.3 M, 0.5 M, or 1 M oxalic acid for 1, 2 or 3 hours at 250°C . PLM analyses showed that the optical properties of asbestos in soils and rocks started were affected by treatment with 0.3 M oxalic acid for 3 hours, 0.5 M oxalic acid for 2 hours, and 1 M oxalic acid for 1 hour at 250°C (Table 3).

The sign of elongation, pleochroism, and dispersion staining of chrysotile-containing soils and rocks were affected by treatment with 1 M oxalic acid and 250°C for 1 hour, but not 0.3 M or 0.5 M oxalic acid (Table 4). The effects of treatment with 1 M of oxalic acid at 250°C , the results of 2, 3-hours were similar to those of 1-hour treatment.

The length and width RIs increased gradually with acid concentration, and the width value differed significantly

Table 2. Changes in the optical characteristics of NOA according to temperature after 3 hours, as determined by PLM.

	Temperature ($^{\circ}\text{C}$)	Sign of elongation	Pleochroism	Extinction	Dispersion staining
S-1 ^{d)}	700	Δ	Δ	\times ^{a)}	Δ ^{b)}
	800	Δ	Δ	\times	\circ ^{c)}
	900	Δ	Δ	\times	\circ
	1000	\circ	Δ	\times	\circ
R-1 ^{e)}	700	\times	\times	\times	\times
	800	\times	\times	\times	Δ
	900	\times	Δ	\times	Δ
	1000	Δ	Δ	\times	\circ

a) \times : no change.

b) Δ : partial change.

c) \circ : change.

d) S-1: chrysotile-containing soil.

e) R-1: chrysotile-containing rock.

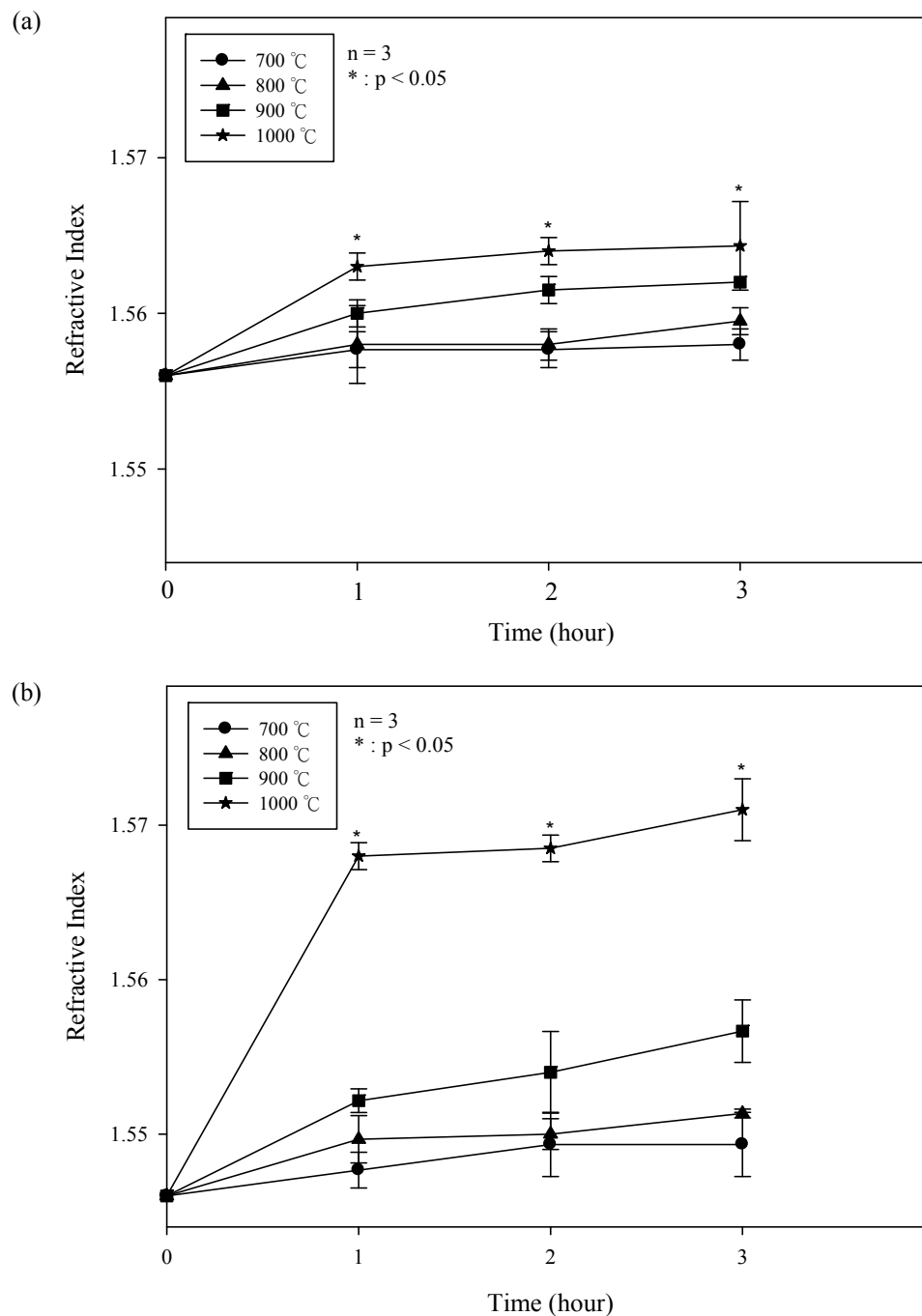


Fig. 2. Changes in the RIs of chrysotile-containing soil according to treatment temperature and time. (a) length, (b) width (n = 3: number of analyses; error bar: standard deviation; length/width: light vibration direction of fiber; $p < 0.05$: t -test compared to the RIs of untreated asbestos).

Table 3. Changes in the optical characteristics of chrysotile-containing soil and rock according to oxalic acid concentration and time at 250°C, as determined by PLM

	0.3 M	0.5 M	1 M
1 hour	×	× ^{a)}	Δ ^{b)}
2 hours	×	Δ	○ ^{c)}
3 hours	Δ	○	○

a) ×: no change.

b) Δ: partial change.

c) ○: change.

Table 4. Changes in the optical characteristics of chrysotile-containing soil and rock according to oxalic acid concentration and time at 250°C, as determined by PLM

Oxalic acid concentration, time	Sign of elongation	Pleochroism	Extinction	Dispersion staining
0.3 M, 1 hour	×	×	×	×
0.5 M, 1 hour	×	×	×	×
1.0 M, 1 hour	Δ	Δ	×	Δ ^{b)}
1.0 M, 2 hours	Δ	Δ	×	○ ^{c)}
1.0 M, 3 hours	Δ	Δ	×	○

a) ×: no change.

b) Δ: partial change.

c) ○: change.

following treatment with 1 M oxalic acid compared to untreated samples (Fig. 3(a)). There was little change according to time following treatment with 1 M oxalic acid at 250°C (Fig. 3(b)).

The results of chrysotile-containing rock differed from those of chrysotile-containing soil, both inside and outside of samples (Table 5). PLM analyses indicated that the optical properties of asbestos inside of samples were unchanged; however, all characteristics—with the exception of extinction—of asbestos on the outside of samples were altered. Both RIs of the outside of samples increased, but those inside of the samples were similar to the values of raw chrysotile (Fig. 4). In the case of width direction, the RI was significantly increased compared to untreated asbestos.

SEM/EDS Analysis

The microstructures of chrysotile-containing soils and rocks were affected by the heat and combination treatments. However, based on the atomic ratio, NOA differed between heat- and combination-treated chrysotile.

SEM showed that the morphology of heat-treated chrysotile changed into an angulated form, while that of the combination-treated chrysotile changed into a conglomerated and harsh form, rather than a long, and winding shape (Fig. 5).

EDS analyses indicated that the atomic ratio of chrysotile was unaffected by heat treatment, but was altered by the combination treatment in both soils and rocks (Table 6). The atomic ratio of combination-treated chrysotile is not included in the references of the Korea Occupational Safety and Health Agency (KOSHA). The results showed lower levels of magnesium and higher levels of silicon compared to untreated samples.

Comparison of Treatment Effects

This study compared the effects of various NOA treatments to identify the optimal treatment conditions. The heat and combination treatments had similar effects on the optical properties of samples; however, their effects on sample composition differed.

The RIs tended to increase in heat- and combination-treated samples compared to untreated chrysotile, based on PLM analyses (Fig. 6). In soil samples, the width RI significantly increased following treatment at both 800°C for 3 hours, and 250°C and 1 M oxalic acid for 1 hour (Fig. 6(a)). In rock samples, the length and width RIs significantly increased

following treatment at 1000°C for 3 hours, and the width value significantly changed following treatment at 250°C with 1 M oxalic acid for 1 hour (Fig. 6(b)).

In soil samples, the atomic ratios of magnesium and silicon showed significant changes following treatment at 250°C and 1 M oxalic acid for 1 hour, but not at 800°C for 3 hours, compared to raw chrysotile (Fig. 7(a)). In rock samples, the atomic ratios of magnesium and silicon also significantly changed following treatment at 250°C with 1 M oxalic acid for 1 hour, but not at 1000°C for 3 hours compared to untreated chrysotile (Fig. 7(b)).

Verification of Treatment Conditions

This study compared the results of other NOA samples to determine the optimal treatment conditions. Sign of elongation, pleochroism, and DS were altered in all chrysotile-containing soils (S-1, S-2, S-3) and rocks (R-1, R-2, R-3) following treatment with 1 M oxalic acid at 250°C for 1 hour. In sample S-2, sign of elongation exhibited a pale blue color at a 45° angle, and extinction showed no bright pattern at any angle (Table 7).

The morphology of the soil (S-2, S-3) and rock (R-2, R-3) samples changed to a conglomerated and harsh form from a long and winding structure based on SEM analyses (Fig. 8). The atomic ratios of chrysotile in soils (S-2, S-3) and rocks (R-2, R-3) are not included in the KOSHA references. All samples showed low levels of magnesium and high levels of silicon compared to untreated samples (Table 8).

DISCUSSION

The aim of this study was to evaluate the effects of various treatments on the physicochemical characteristics of NOA and to identify the optimal treatment conditions. The changes in asbestos properties differed according to NOA type and treatment method, and 1 M oxalic acid at 250°C for 1 hour was the optimal condition for treatment of chrysotile-containing soils and rocks. We performed heat treatments, as well as simultaneous heat and acid combination treatments to alter the characteristics of asbestos at lower temperatures. Oxalic acid was selected for the combination treatment because it is effective for dissolving chrysotile (Rozalen and Huertas, 2013). PLM and SEM/EDS were applied to examine the optical, morphological, and chemical properties of the samples.

First, the optical properties—sign of elongation, pleochroism (color), RI (dispersion staining), and extinction—of NOA were evaluated by PLM. Pleochroism appeared gradually after both heat and combination treatments,

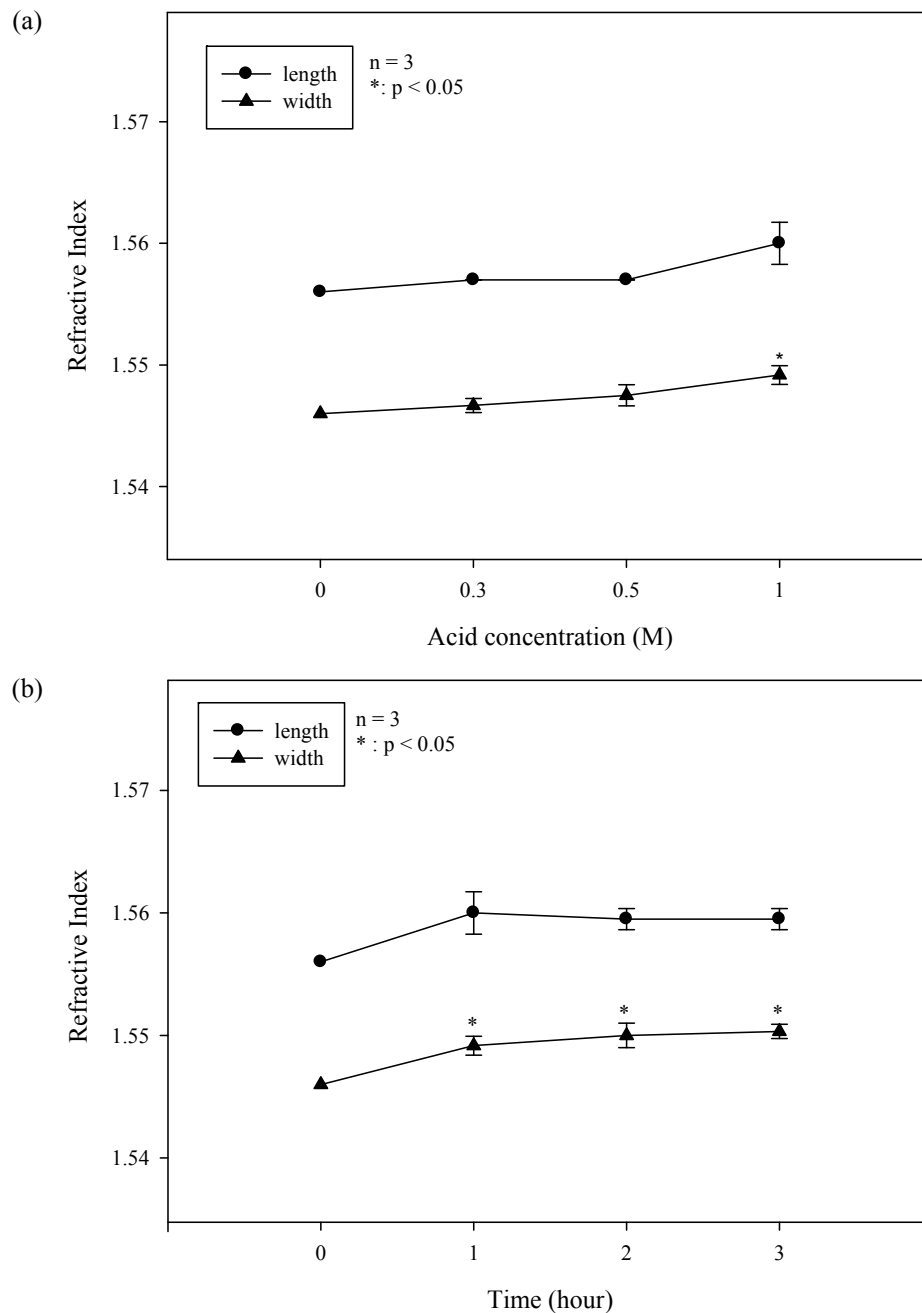


Fig. 3. Change in the RIs of chrysotile-containing soil at 250°C according to (a) acid concentration for 1 hour and (b) time with 1 M oxalic acid (n = 3: number of analyses; error bar: standard deviation; length/width: light vibration direction of fiber; $p < 0.05$: t -test compared to the RIs of untreated asbestos).

Table 5. Changes in the optical characteristics on the inside and outside of chrysotile-containing rock following treatment with 1 M oxalic acid at 250°C for 1 hour, as determined by PLM.

	Sign of elongation	Pleochroism	Extinction	Dispersion staining
Inside	×	×	×	× ^{a)}
Outside	Δ	Δ	×	Δ ^{b)}

a) ×: no change.

b) Δ: partial change.

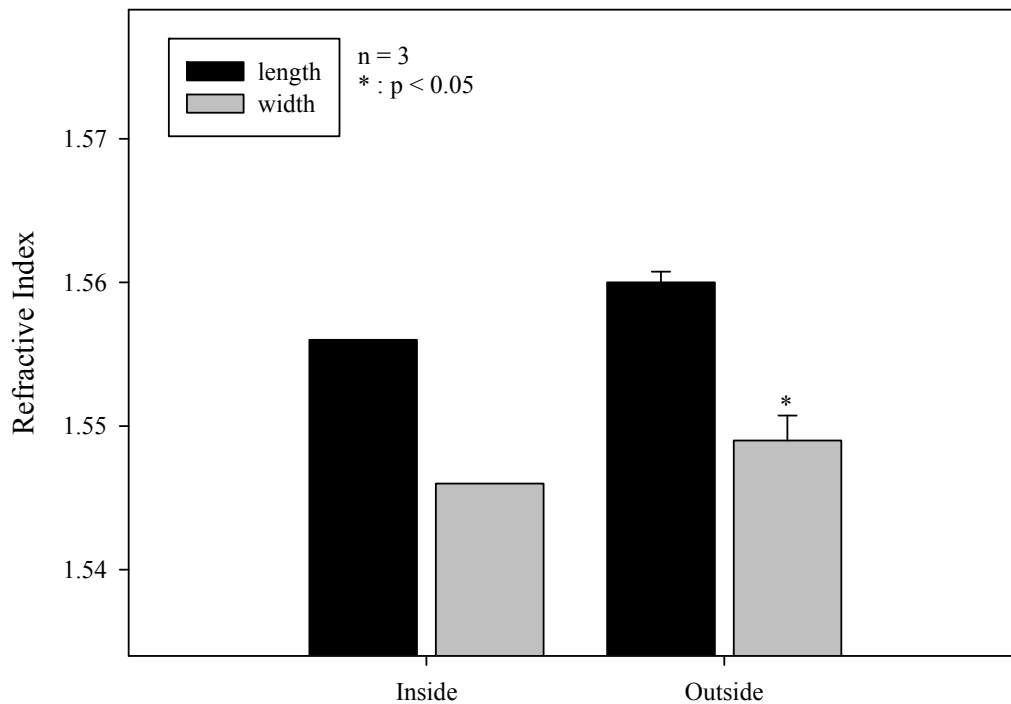
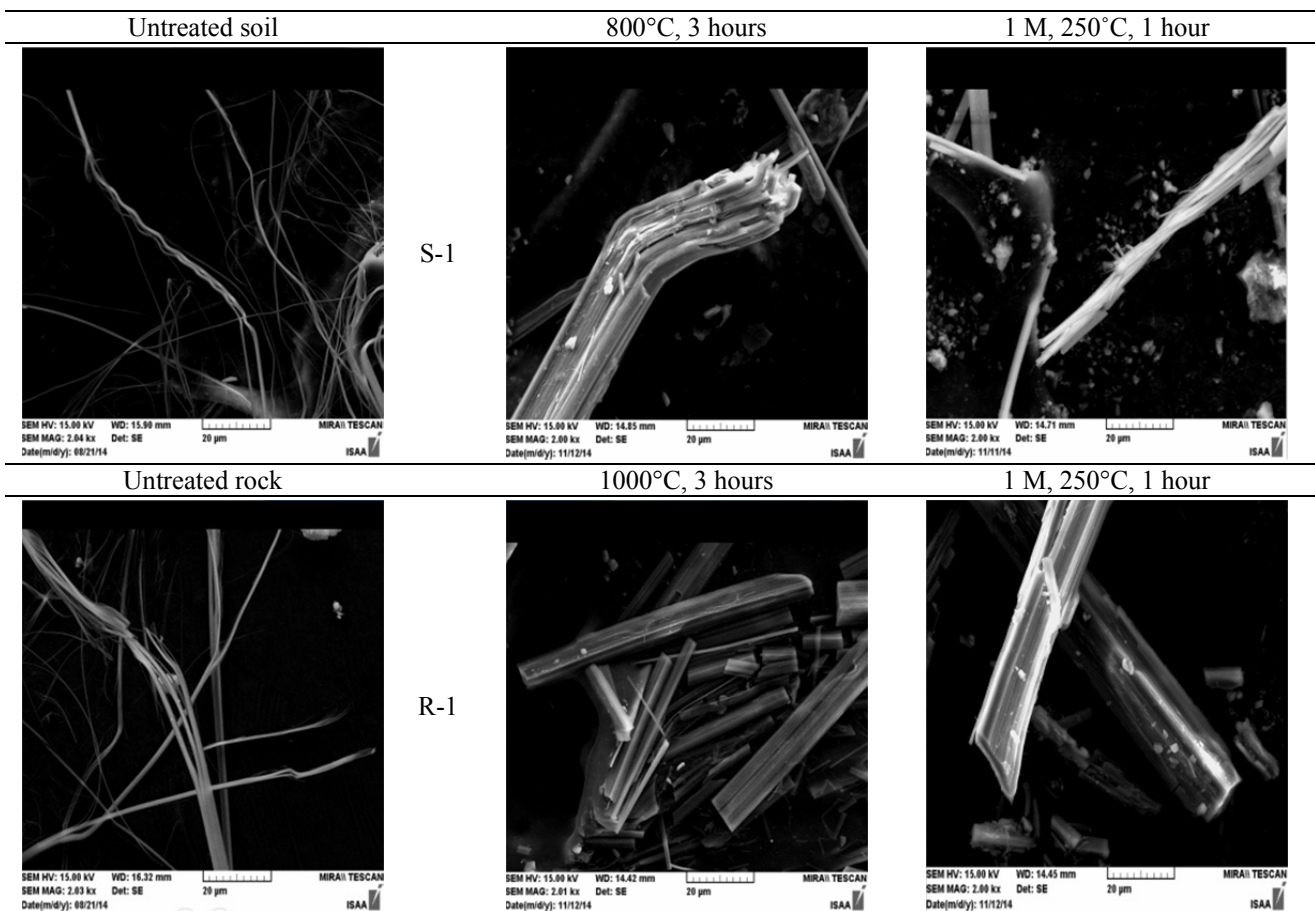


Fig. 4. RIs of the insides and outsides of chrysotile-containing rock samples ($n = 3$: number of analyses; error bar: standard deviation; length/width: light vibration direction of fiber; $p < 0.05$: t -test compared to the RIs of untreated asbestos).



※ Note: magnification = $2,000\times - 1$; SEM HV: 15.00 kV; WD: 15.00 mm.

Fig. 5. SEM images (S-1, R-1) of NOA morphology before and after treatments.

Table 6. Comparison of the elemental compositions of chrysotile-containing soils and rocks with the KOSHA reference after heat treatment.

%	KOSHA criteria for asbestos	S-1		R-1	
		800°C, 3 hours	250°C, 1 M, 1 hour	1000°C, 3 hours	250°C, 1 M, 1 hour
Mg	52.0 ± 3.5	49.85 ± 0.28	19.92 ± 3.60	49.87 ± 1.32	6.53 ± 10.97
Si	45.9 ± 3.4	48.89 ± 0.42	78.66 ± 4.13	48.89 ± 1.30	92.23 ± 10.88
Fe	2.1 ± 0.9	1.26 ± 0.15	1.42 ± 0.46	1.24 ± 0.20	1.24 ± 0.12
Judgment compared to the KOSHA criteria		Not changed	Changed	Not changed	Changed

※ Note: Elemental composition of chrysotile according to the Korea Occupational Safety and Health Agency: Mg: 52.0 ± 3.5%, Si: 45.9 ± 3.4%, Fe: 2.1 ± 0.9%.

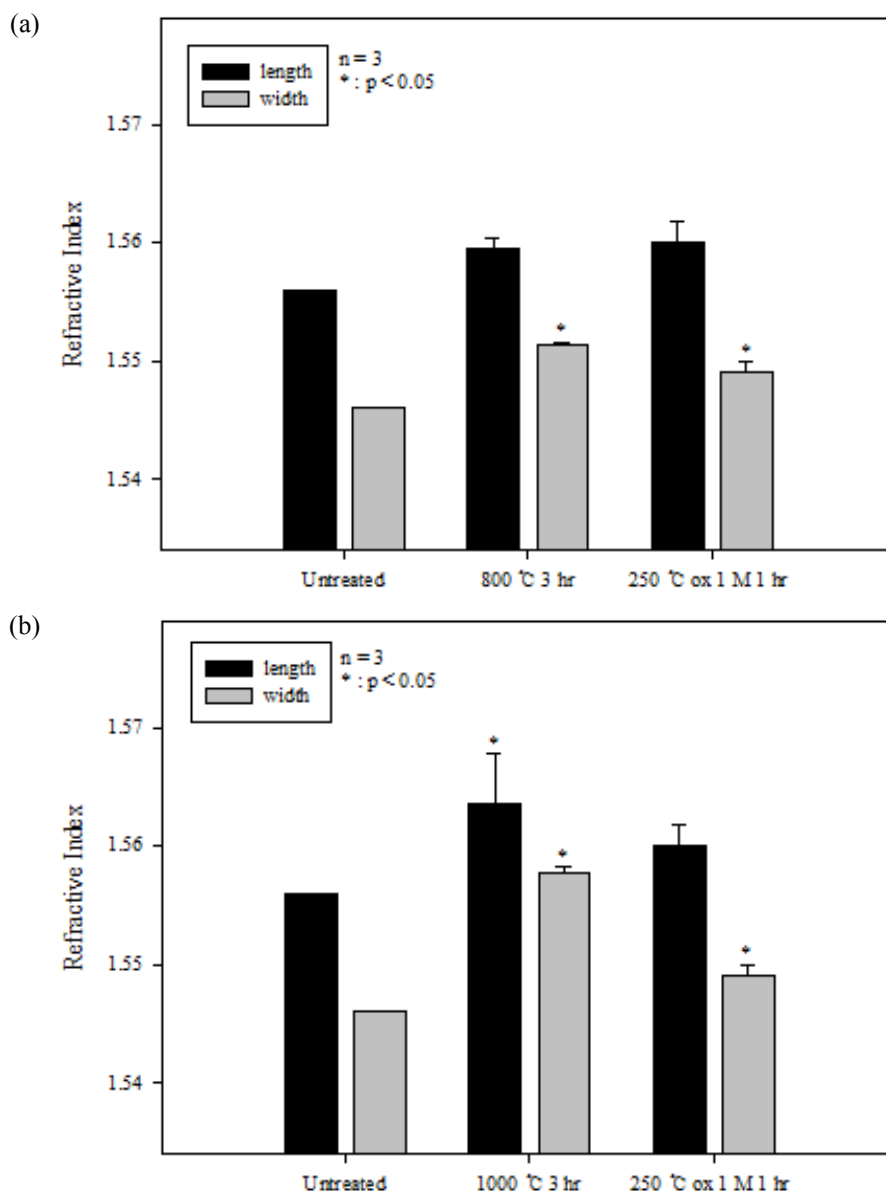


Fig. 6. Comparison of RIs according to treatment conditions, as determined by PLM. (a) Chrysotile-containing soil (S-1) (b) chrysotile-containing rock (R-1) (n = 3: number of analyses; error bar: standard deviation; length/width: light vibration direction of fiber; $p < 0.05$: t -test compared to the RIs of untreated asbestos).

although raw chrysotile has no color at any angle. These results suggested that the patterns of absorption and

transmission of light within fibers were changed. RIs according to light vibration direction also increased after

both treatments, which indicated that the fiber density was increased. Chrysotile in soil exhibits positive elongation, but changed to negative elongation following treatment at 1000°C. In the case of chrysotile in rock, the optical properties were altered at 1000°C but elongation remained positive. Other studies have also reported reversal of signs of elongation at high temperature (Laughlin and McCrone, 1989; Prentice and Keech, 1989), which indicates that the RI and density of the width direction are higher than those of the length direction within the fiber. Notably, following the combination treatment, some asbestos exhibited a pale color, similar to bleached fiber. This result corresponds to a

report of a pale blue color in the 2–8 o'clock position (Nam *et al.*, 2014). Chrysotile is the lightest at the 45° angle, and its color disappears at the 90° angle upon extinction. While the extinction properties were unaffected by treatment at 1000°C, the bright color partially disappeared at 45°, resulting in a pale-colored fiber as was the case following the combination treatment. Regarding the principle of extinction, it is estimated that the fiber changed from an anisotropic to an isotropic mineral having one light direction (Eller and Cassinelli, 1994). The extinction angle can be used to distinguish asbestiform from non-asbestiform minerals, which are often found in mixed mineral environments (Lee *et al.*, 2008).

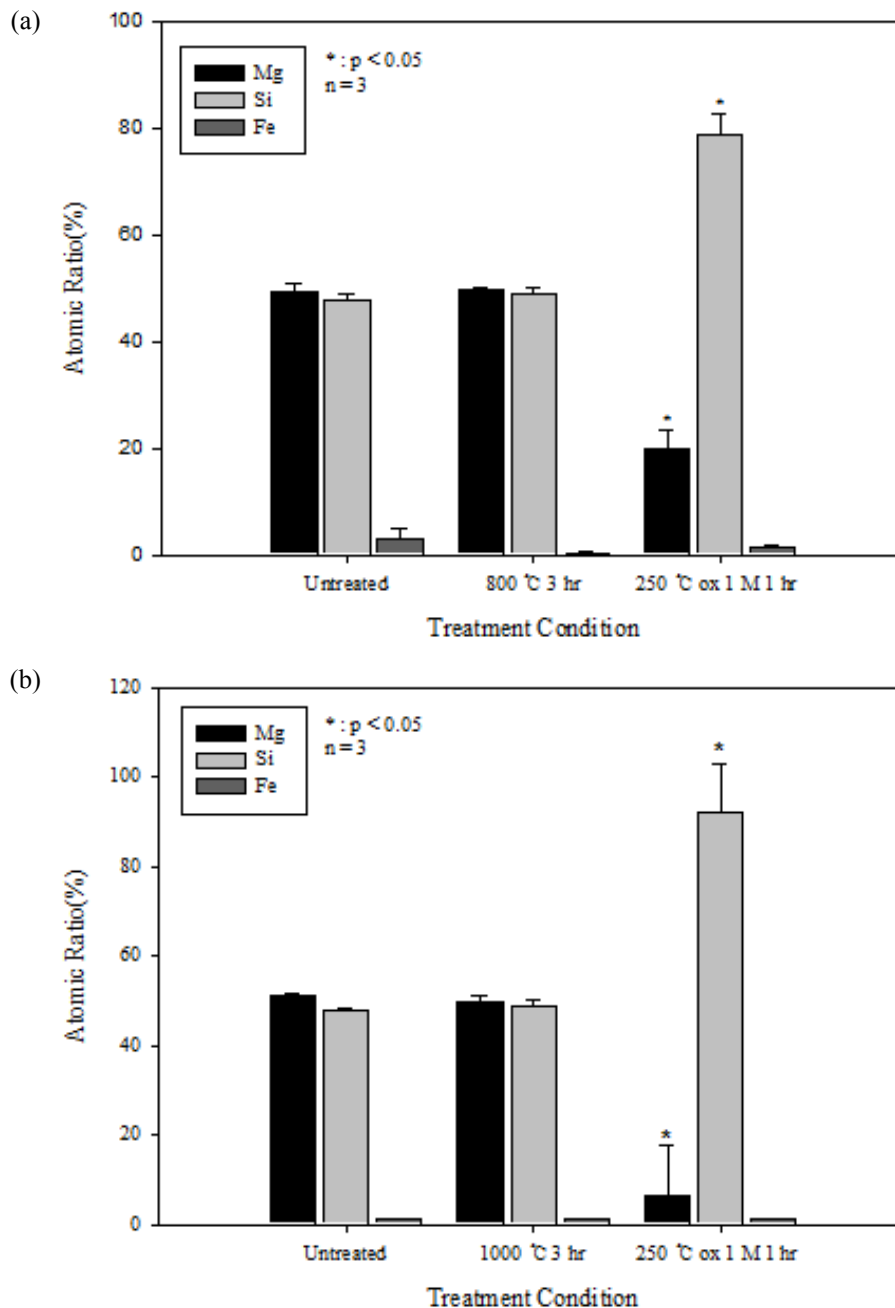


Fig. 7. Comparison of compositional changes according to treatment conditions, as determined by EDS. (a) Chrysotile-containing soil (S-1), (b) chrysotile-containing rock (R-1) ($n = 3$: number of analyses; error bar: standard deviation; $p < 0.05$: t -test compared to the atomic ratios of untreated asbestos).

Table 7. Comparison of the effects of treatment at 250°C with 1 M oxalic acid for 1 hour on chrysotile-containing soils and rocks according to sample number.

	Sign of elongation	Pleochroism	Extinction	Dispersion staining
S-1 ^{e)}	Δ	Δ	× ^{a)}	Δ ^{b)}
S-2 ^{e)}	○ ^{c), d)}	Δ	○	○ ^{c)}
S-3 ^{e)}	Δ	Δ	×	○
R-1 ^{f)}	Δ	Δ	×	Δ
R-2 ^{f)}	Δ	Δ	×	Δ
R-3 ^{f)}	Δ	Δ	×	Δ

a) ×: no change.

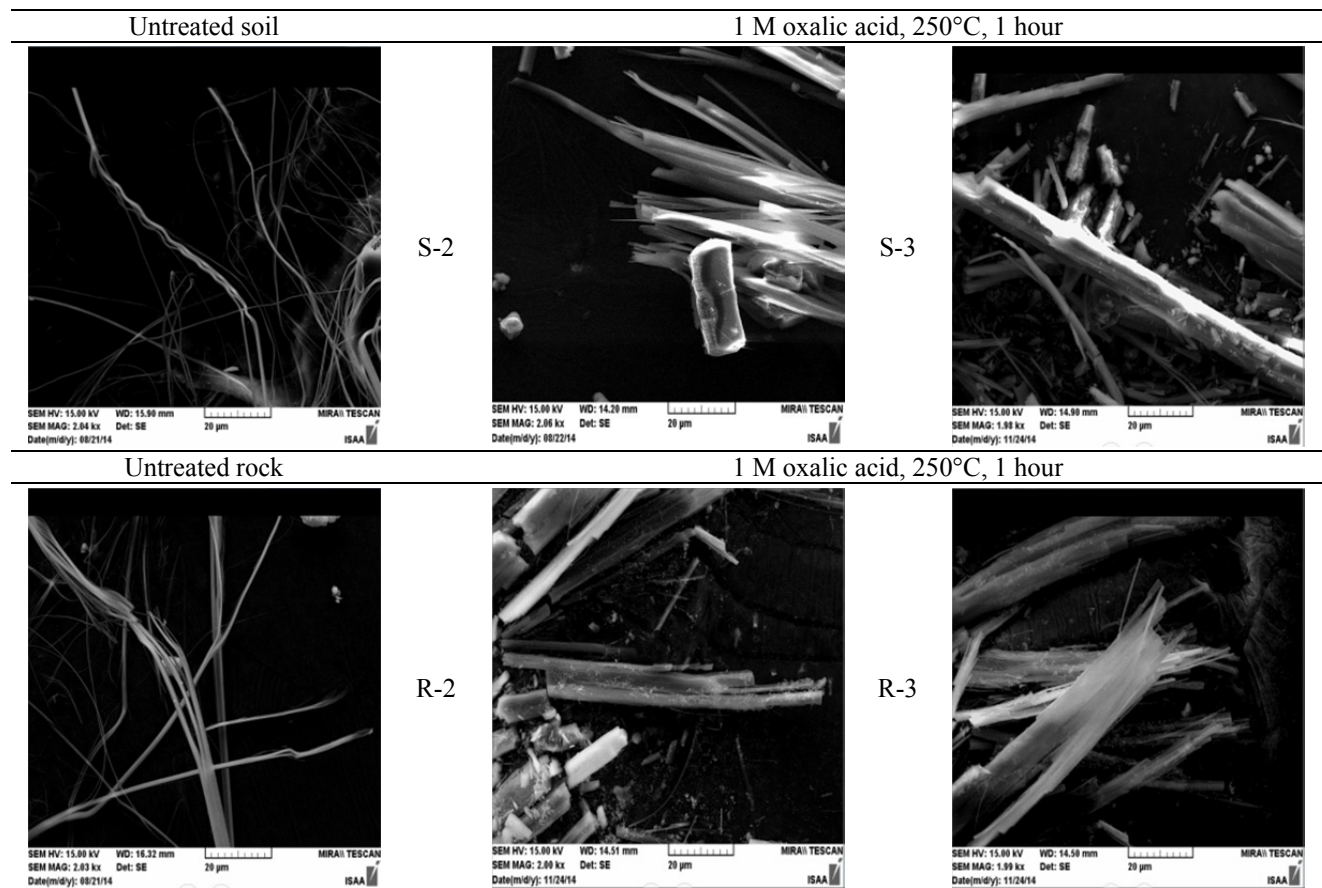
b) Δ: partial change.

c) ○: change.

d) Pale color.

e) S-1, 2, 3: chrysotile-containing soils.

f) R-1, 2, 3: chrysotile-containing rocks.



※ Note: magnification = 2,000× – 1; SEM HV: 15.00 kV; WD: 15.00 mm.

Fig. 8. SEM images of the morphologies of chrysotile-containing soils (S-2, S-3) and rocks (R-2, R-3) before and after combination treatment.

Four optical characteristics of asbestos were examined to determine whether RIs differed between treated and untreated samples. After heat treatment, NOA exhibited changes at a higher temperature than asbestos fibers. Chrysotile fiber was altered at 700°C for 3 hours (Moon, 2014), but chrysotile in soil began to show changes at 800°C due to the presence of other materials either mixed with or covering the asbestos. For a notable optical change, chrysotile-containing soil

required a temperature of ~1000°C. On the other hand, chrysotile in rock was unaffected by treatment at 1000°C because the asbestos fiber was embedded deeply in the rock. After combination treatment, NOA started to exhibit changes following treatment with 1 M oxalic acid at 250°C for 1 hour. In the case of chrysotile fiber, the optical properties changed following treatment with 0.3 M oxalic acid at 200°C for 1 hour (Moon, 2014). However, chrysotile in soil and

Table 8. Comparison of the elemental compositions of chrysotile-containing soil (S-2, S-3) and rock (R-2, R-3) with the KOSHA reference criteria after combination treatment.

%	KOSHA	S-2	S-3	R-2	R-3
	criteria for asbestos	250°C, 1 M oxalic acid, 1 hour			
Mg	52.0 ± 3.5	0.68 ± 0.18	8.95 ± 2.05	2.53 ± 2.37	3.16 ± 0.90
Si	45.9 ± 3.4	99.21 ± 2.47	89.51 ± 1.86	96.84 ± 2.71	95.99 ± 0.70
Fe	2.1 ± 0.9	2.47 ± 0.26	1.54 ± 1.62	0.62 ± 0.35	0.85 ± 0.20
Judgment compared to the KOSHA criteria		Changed	Changed	Changed	Changed

※ Note: Elemental composition of chrysotile according to the Korea Occupational Safety and Health Agency: Mg: 52.0 ± 3.5%, Si: 45.9 ± 3.4%, Fe: 2.1 ± 0.9%

rock required higher acid concentrations and temperatures, although there was little change according to time.

Second, the morphologies and chemical properties of samples were evaluated by SEM/EDS to identify changes in asbestos properties. Based on SEM analysis, after heat treatment, the surface morphology of asbestos changed from a thin and silky shape, similar to a thread, to an angulated form, similar to a piece of wood, according to the temperature used. After combination treatment, chrysotile fiber exhibited a conglomerated shape and a greater surface roughness than untreated fiber. PLM analysis suggested these results be related to the increased RIs, because the density of fiber was shown to increase after the heat and combination treatments.

Based on EDS analysis, heat-treated samples were characterized as chrysotile according to the KOSHA reference, and showed no significant change compared to untreated samples. On the other hand, combination-treated samples showed a dramatically increased atomic ratio of silicon. This indicates that magnesium and iron were emitted from the asbestos structure after the hydrolysis reaction between asbestos and acid. Oxalic acid, which was used in this study, dissolves brucite layers ($[\text{Mg}_3\text{O}_2(\text{OH})_4]_{\text{n}}^{2\text{n}+}$) and reacts more rapidly with increasing concentration, precipitating glushinskite (Rozalen and Huertas, 2013). While heat-treated asbestos transforms to forsterite at temperatures higher than 500°C (Jeyaratnam and West, 1994), our data indicate that this is not a chemical change related to atomic ratio, but simply a change in crystalline structure causing a change of optical properties. It has been reported that the human toxicity of asbestos is caused by physical and chemical factors (Nam et al., 2014). Heat treatment was effective in transforming the physical characteristics, but not the elemental composition, of asbestos. On the other hand, combination treatment yielded changes in the morphological, compositional, and optical characteristics of asbestos at lower temperatures than heat treatment alone.

We assessed the reduction ratios of magnesium and iron by evaluating the increased ratio of silicon. This was because asbestos has a basic silicate framework in which keep silicate layer inside and brucite layer outside of the fibers (Fubini and Areal, 1999). From a toxicological viewpoint, asbestos treatment focuses on the magnesium concentration in chrysotile and the iron concentration in amphibole. This is because biological conditions facilitate emission of metal ions such as iron in amphiboles and magnesium in chrysotile. However, iron concentration is one of the most important

factors in toxicity (Fubini and Areal, 1999). Therefore, methods for the complete removal of iron from asbestos should be developed, and methods for accurate measurement of metal ion contents should be developed to overcome the large variations inherent to EDS analyses.

Acid concentration is the most important of the three factors in the combination treatment. Following treatment at 250°C for 1 hour, the optical properties changed in the presence of 1 M oxalic acid, but not 0.3 or 0.5 M. The width RI began to exhibit significant differences at 1 M oxalic acid, and changed little with increased treatment duration. It is hypothesized that chemical digestion occurred through release of hydrogen ions due to the acid reacting with the surface of the chrysotile in the soils and rocks (Jeyaratnam and West, 1994; Teir et al., 2007). Following this reaction, magnesium is extracted from the asbestos structure (Jeyaratnam and West, 1994; Teir et al., 2007). In the preliminary assessment of the combination treatment, NOA did not exhibit changes at temperatures < 200°C for short treatment durations. The magnesium extraction rate increased with increasing temperature (Nam et al., 2014). This suggested that the reaction is accelerated at higher temperatures and so NOA should be treated at temperatures above 200°C to obtain effective results within limited treatment durations. Heat and acid should be applied simultaneously because this shortens the treatment duration to 1 hour, while acid-only treatment requires at least 5 days (Jeong and Han, 2014). In another study, the combination of oxalic acid and ultrasonic vibrations was shown to require over 12 hours of treatment (Turci et al., 2010). To our knowledge, few studies have used simultaneous heat and acid treatment of NOA. In this study, 1 hour of oxalic acid treatment at a low temperature was demonstrated to alter the chrysotile in soils and rocks.

From a practical perspective, combination treatment can reduce much cost and time which caused by heat-only treatment. Also, combination method would alter the atomic ratio which related to carcinogenic mechanisms of asbestos. In case of treating ACMs, it is easier to apply the combination method than treating NOA, because most ACMs are chrysotile which has weaker acid-resistance than other types of asbestos. Currently, disposal of asbestos-containing materials is not a perfect alternative to avoidance of exposure to asbestos. NOA distribution areas occupy approximately 6% of Korea according to a geological map produced by the Ministry of Environment. This study was focused on

reducing the hazard posed by NOA, and also important for exposure management and prevention of secondary exposure. In this study, field samples of only chrysotile-containing soils and rocks were analyzed. However, amphiboles are more common than chrysotile in the natural environment, comprising about 5% of Earth's crust (Dyar *et al.*, 2008). Moreover, amphibole asbestos is more hazardous than chrysotile (McDonald *et al.*, 2004). Amphibole asbestos thermally decomposes at higher temperatures and its acid resistance is greater than that of chrysotile (Jeyaratnam and West, 1994). Therefore, another agent or combination method should be considered to treat this type of NOA.

The first limitation of this study is its application to mass quantities of NOA, reflecting real treatment situations, because only small amounts of asbestos were used in this study. The optimal treatment condition does not represent a universal method, because the results varied according to sampling location. Therefore, further studies in which other determinants, such as soil taxonomy and size of rock, are taken into consideration should be conducted. Second, a quantitative measuring technique is required to determine morphological changes in asbestos, because the toxicity is caused by both chemical and physical factors of the fiber. Also, the physicochemical characteristics of asbestos related to the changes in optical properties should be identified. Third, the characteristics of asbestos inside the chrysotile-containing rocks were unaffected, even following the combination treatment. Therefore, a further method for processing of asbestos-containing rock is required, such as grinding. Finally, no toxicological assessment was conducted, although the properties of asbestos were changed. However, the results of this study will provide valuable information for further research aiming to improve NOA disposal methods.

CONCLUSIONS

The optimal NOA treatment condition was 1 M oxalic acid at 250°C for 1 hour. Combination treatment resulted in changes in asbestos properties at lower temperatures than heat-only treatment and yielded changes in the morphological, chemical, optical characteristics. The results of this study provide an efficient method for management and disposal of NOA at reduced cost and time. In addition, this study clearly demonstrates the different changing patterns in chemical properties of chrysotile between heat and combination treatment.

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